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The Second Law of Thermodynamics

and Cyclic Processes

by

A. E. Green and P. M. Naghdi

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The Second Law of Thermodynamics

and Cyclic Processes

by

A. E. Green[†] and P. M. Naghdi[‡]

Abstract.   This paper is concerned with the implications of an inequality
proposed recently by Green and Naghdi [3] in regard to the classical statements
of the second law of thermodynamics associated with cyclic thermo-mechanical
processes.   The results obtained are compared with corresponding previous
developments by Fosdick and Serrin [1] and by Truesdell [2] who employ the
Clausius-Duhem inequality.

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1.   Introduction

In two recent papers, Fosdick and Serrin [1] and Truesdell [2] have con-
sidered a continuous deformable body in contact with a reservoir of heat whose
temperature is homogeneous but one which may vary with time; and after stipu-
lating (i) heat transfer inequalities for heat flow between the body and the
reservoir and (ii) certain conditions for cyclic processes, with the use of
the global Clausius-Duhem inequality, they prove in the words of Truesdell
"..strictly and trivially, the four commonest traditional statements of the
second law as proclamations of impossibility..." These proofs are independent
of particular constitutive assumptions so that the results apply to all single
phase continua of classical type. Also, Fosdick and Serrin [1] remark that
"...the Clausius-Duhem inequality turns out to be consistent with these
classical statements,..., and adds a further degree of credibility to the
Clausius-Duhem inequality beyond its degree of successful application in
other directions of continuum mechanics." In his concluding comments,
Truesdell [2] states "Perhaps the Clausius-Duhem inequality expresses more
that the second law...In time, as rational thermodynamics becomes more
widely applied and more deeply studied, the Clausius-Duhem inequality may
be weakened. But, after the spectacular success gained by use of it, I
doubt it will ever be discarded."

Despite the claim of impressive support for the Clausius-Duhem inequality,
some doubts have been already expressed regarding its validity for all
single phase materials. Even the generality of the above mentioned proofs
of the four traditional statements of the second law should give rise to
some concern. The possibility that the Clausius-Duhem inequality may lead
sometimes to more, and sometimes to less, than is required by the second law
has been demonstrated in [3, Sec. 7]. Moreover, in [3] the present authors
have proposed: (a) a new approach to continuum thermomechanics, which is

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independent of any particular mathematical expression of the second law; and (b) a new inequality representing the second law, which reflects the fact that for every process associated with a dissipative material, a part of the mechanical work is always converted into heat and this cannot be withdrawn from the medium as mechanical work.

In view of the work of Fosdick and Serrin [1] and of Truesdell [2] outlined above, it is of interest to see what can be said about the classical statements with the use of the inequality proposed in [3]. This is the main purpose of the present note. To conserve space and for ease of comparison, in the next two sections, we adhere to the notations and mode of approach to the subject adopted in [1,2].

2. General background

We summarize here some definitions and formulae from the papers of Fosdick and Serrin [1] and of Truesdell [2]. Consider a body $\mathcal{B}$ consisting of particles X and endowed with a continuous mass measure m. Let $\mathcal{B}_t$ denote the configuration of $\mathcal{B}$ at time t bounded by a closed surface $\partial\mathcal{B}_t$ whose outward unit normal is $\underset{\sim}{n}$. Further, let $\epsilon(X,t)$, $\eta(X,t)$, $\underset{\sim}{v}(X,t)$, $\underset{\sim}{t}(X,t)$, $\underset{\sim}{b}(X,t)$, $\underset{\sim}{q}(X,t)$, $r(X,t)$ denote, respectively, the internal energy per unit mass, the entropy per unit mass, the velocity, the traction on $\partial\mathcal{B}_t$, the external body force density, the heat flux vector at any point in $\mathcal{B}$, the external rate of supply of heat per unit mass. With reference to the configuration of $\mathcal{B}$ at time t, we define the internal energy E, the kinetic energy K, the rate of work W by body force and by surface tractions and the total external supply of heat Q by

$$E(\mathcal{B}_t) = \int_{\mathcal{B}_t} \epsilon \, dm \quad , \quad K(\mathcal{B}_t) = \int_{\mathcal{B}_t} \tfrac{1}{2} \underset{\sim}{v} \cdot \underset{\sim}{v} \, dm \quad ,$$

$$W(\mathcal{B}_t) = \int_{\mathcal{B}_t} \underset{\sim}{b} \cdot \underset{\sim}{v} \, dm + \int_{\partial\mathcal{B}_t} \underset{\sim}{t} \cdot \underset{\sim}{v} \, da \quad , \tag{1}$$

$$Q(\mathcal{B}_t) = \int_{\mathcal{B}_t} r \, dm - \int_{\partial\mathcal{B}_t} \underset{\sim}{q} \cdot \underset{\sim}{n} \, da \quad ,$$

where dm is the mass element and da the element of area.

In the discussion that follows, the body $\mathcal{B}$ is assumed to be immersed in a heat reservoir $\mathcal{R}$ whose absolute temperature $\tau(t) > 0$ is spatially homogeneous and depends on time only. We consider piecewise differentiable processes undergone by $\mathcal{B}$ during a finite time interval $\mathcal{I} = [t_1, t_2]$ and denote by $\mathcal{I}^+ \subseteq \mathcal{I}$ and $\mathcal{I}^- \subseteq \mathcal{I}$ those intervals of time $\mathcal{I}$ during which $Q(\mathcal{B}_t) > 0$ or $Q(\mathcal{B}_t) < 0$, respectively. The body absorbs heat or emits heat at time t according to $Q(\mathcal{B}_t) > 0$ or $Q(\mathcal{B}_t) < 0$, respectively, and the corresponding total heat absorbed and emitted are C^+ and C^- with

$$C^+ = \int_{\vartheta^+} Q(\mathcal{B}_t)dt \quad , \quad C^- = -\int_{\vartheta^-} Q(\mathcal{B}_t)dt \quad . \tag{2}$$

The net work done by $\mathcal{B}$ during the time interval ϑ is given by

$$U = -\int_{\vartheta} W(\mathcal{B}_t)dt \quad . \tag{3}$$

The first law of thermodynamics for the body $\mathcal{B}$ may now be stated as

$$U + \Delta E + \Delta K = C^+ - C^- \quad , \tag{4}$$

where the prefix Δ denotes the "difference" operation on functions during the time interval ϑ.

The papers by Fosdick and Serrin [1] and by Truesdell [2] express the view that "heat...never passes out of a body except when it flows by conduction or by radiation into a colder body" and postulate the inequalities

$$(\theta - \tau)\underset{\sim}{q} \cdot \underset{\sim}{n} \geqq 0 \quad \text{on} \quad \partial\mathcal{B}_t \quad ,$$

$$(\theta - \tau)r \leqq 0 \quad \text{in} \quad \mathcal{B}_t \quad , \tag{5}$$

where $\theta(X,t)$ is the absolute temperature of the body. It should be kept in mind that while the absolute temperature of the heat reservoir $\tau(t)$ is spatially homogeneous, the absolute temperature of the body $\theta(X,t)$ may depend on the particular particle as well as on time.

In the interior of the body, the direction of the heat flow is determined by the heat flux vector $\underset{\sim}{q}$ alone. Supplementary to the conditions (5), we also require that heat never flows across any surface in the body except when it flows from a hotter to a colder part and interpret this by the classical inequality

$$-\underset{\sim}{q} \cdot \underset{\sim}{g} \geqq 0 \quad , \tag{6}$$

where $\underset{\sim}{g}(X,t)$ is the temperature gradient in the body.

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Although for many materials the inequality (6) follows from the Clausius-Duhem inequality, it does not follow for all materials. Indeed, it has often been emphasized in the literature that the Clausius-Duhem inequality may permit heat to flow from a cold to a hot part of a body. Fosdick and Serrin [1], as well as Truesdell [2], introduce no restriction of the form (6) in their works. We return to this point later.

3. Cyclic motions

In addition to the temperature $\theta(X,t)$ and the temperature gradient $\underset{\sim}{g}(X,t)$ introduced in section 2, let $\underset{\sim}{F}(X,t)$ be the deformation gradient at any point in $\mathcal{B}$ measured relative to some reference configuration. Also, let $\underset{\sim}{D}(X,t)$ and $\underset{\sim}{T}(X,t)$ denote the rate of deformation and the Cauchy stress tensor, respectively. As in the paper of Green and Naghdi [3], we assume that the constitutive response functions for ϵ, η include dependence on the set of variables $\dot{\underset{\sim}{F}}, \dot{\theta}, \underset{\sim}{g}$ and their higher space and time derivatives and refer to this set collectively as υ, where a superposed dot denotes the material time derivative. Further, let ϵ', η' be the respective values of ϵ, η when the variables υ are set equal to zero in the response functions. Thus, for example,

$$\epsilon = \epsilon(\underset{\sim}{F}, \theta, \upsilon) \quad , \quad \epsilon' = \epsilon'(\underset{\sim}{F}, \theta) = \epsilon(\underset{\sim}{F}, \theta, 0) \quad , \quad \upsilon = (\dot{\underset{\sim}{F}}, \dot{\theta}, \underset{\sim}{g}, \ldots) \quad , \tag{7}$$

where the dots in $(7)_3$ refer to the higher space and time derivatives of $\dot{\underset{\sim}{F}}, \dot{\theta}, \underset{\sim}{g}$. Then, from the paper of Green and Naghdi [3], we have

$$\rho r - \text{div } \underset{\sim}{q} = \rho \theta \dot{\eta}' + \rho(\dot{\epsilon} - \dot{\epsilon}') - \rho w \quad ,$$

$$\rho w = -\rho(\dot{\epsilon}' - \theta \dot{\eta}') + \underset{\sim}{T} \cdot \underset{\sim}{D} \quad . \tag{8}$$

In a manner similar to that of Fosdick and Serrin [1] and of Truesdell [2], we may use (8) to rewrite the energy equation (4) in the form

$$U = (1 - \frac{a}{b})C^+ - (\Delta E + \Delta K - a \Delta H^*)$$

$$- a\{\int_{\mathscr{I}^+} (\frac{1}{\tau} - \frac{1}{b})Q(\mathcal{B}_t)dt + \int_{\mathscr{I}^-} (\frac{1}{a} - \frac{1}{\tau})[-Q(\mathcal{B}_t)]dt$$

$$+ \int_{\mathscr{I}^+} [\int_{\mathcal{B}_t} (\frac{1}{\theta} - \frac{1}{\tau})r \ dm - \int_{\partial \mathcal{B}_t} (\frac{1}{\theta} - \frac{1}{\tau})\underset{\sim}{q} \cdot \underset{\sim}{n} \ da]$$

$$+ \int_{\mathscr{I}} \int_{\mathcal{B}_t} (-\frac{\underset{\sim}{q} \cdot \underset{\sim}{g}}{\rho \theta^2} + \frac{w}{\theta})dm \ dt\} \quad , \tag{9}$$

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where a and b are arbitrary constants and

$$H^*(\mathcal{B}_t) = H'(\mathcal{B}_t) + \int_{\mathcal{I}}\int_{\mathcal{B}_t} \frac{\dot{\epsilon} - \dot{\epsilon}'}{\theta} \, dm \, dt \quad , \quad H'(\mathcal{B}_t) = \int_{\mathcal{B}_t} \eta' \, dm \quad . \tag{10}$$

We recall now the mathematical expression of the second law of thermodynamics proposed by Green and Naghdi [3], namely

$$w \geqq 0 \tag{11}$$

for all thermo-mechanical processes. In view of the inequalities (5), (6) and (11), it follows from (9) that for all positive constants a and b,

$$U \leqq (1 - \frac{a}{b})C^+ - (\Delta E + \Delta K - a\Delta H^*)$$

$$- a\{\int_{\mathcal{I}^+} (\frac{1}{\tau} - \frac{1}{b})Q(\mathcal{B}_t)dt + \int_{\mathcal{I}^-} (\frac{1}{a} - \frac{1}{\tau})[-Q(\mathcal{B}_t)]dt\} \quad . \tag{12}$$

In particular, if $a = \tau_{min}$ and $b = \tau_{max}$, where τ_{min} and τ_{max} are the infimum and supremum of $\tau(t)$ over $\mathcal{I}$, then

$$U \leqq (1 - \frac{\tau_{min}}{\tau_{max}})C^+ - (\Delta E + \Delta K - \tau_{min}\Delta H^*) \quad . \tag{13}$$

This is similar to the inequality obtained by Fosdick and Serrin [1] and by Truesdell [2], except that on the right-hand side of their inequality corresponding to (13) they have

$$H(\mathcal{B}_t) = \int_{\mathcal{B}_t} \eta \, dm \tag{14}$$

instead of H^* defined by $(10)_1$.

In special cases in which the constitutive response functions for ϵ, η do not depend explicitly on the variables υ so that

$$\epsilon' = \epsilon \quad , \quad \eta' = \eta \tag{15}$$

and

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$$E'(\mathcal{B}_t) = \int_{\mathcal{B}_t} \epsilon' \, dm \quad , \quad H^* = H' = H \quad , \tag{16}$$

the inequality (13) reduces to the corresponding inequality in the papers of Fosdick and Serrin [1] and Truesdell [2] but the range of validity of our inequality (13) under the conditions (16) is limited to the class of materials specified by (15).

Fosdick and Serrin [1] and Truesdell [2] define cyclic processes as those for which

$$\Delta K = 0 \quad , \quad \Delta E = 0 \quad , \quad \Delta H = 0 \quad , \tag{17}$$

although as Truesdell [2] remarks, "this is not a definition but a consequence of particular constitutive relations...so that this definition to some extent begs the question." In fact, the simultaneous requirement $(17)_{2,3}$ for all materials undergoing a cyclic change of deformation and temperature may not be possible. With the above conditions (17), Fosdick and Serrin [1], as well as Truesdell [2], observe that

$$C^+ - C^- = U \leqq (1 - \frac{\tau_{min}}{\tau_{max}})C^+ \tag{18}$$

and they prove the following four statements:

Statement 1. A cycle cannot absorb heat unless it also emits heat.

Statement 2. A cycle that emits no heat cannot do positive work.

Statement 3. A cycle that absorbs and emits heat only at a finite number of temperatures, such that at all of these except one the heat emitted equals the heat absorbed, cannot do positive work.

Statement 4. If a cycle absorbs heat only at a temperature not greater than those at which it emits heat, it cannot do positive work.

The proof of the above statements utilizes the inequalities (5), the global Clausius-Duhem inequality and the conditions (17) and the statements are intended

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to apply to all materials regardless of their constitutive response. On the other hand, the same results follow from the inequality (11) proposed by Green and Naghdi [3] and the conditions (5) and (6) for the restricted class of materials specified by (15) provided

$$\Delta K = 0 \quad , \quad \Delta E' = 0 \quad , \quad \Delta H' = 0 \quad , \tag{19}$$

where E' and H' are defined by $(16)_1$ and $(10)_2$, respectively. For this class of materials, the heat conduction inequality (6) and the inequality (11) imply the local Clausius-Duhem inequality but not conversely. The inequality (11) arises only from consideration of restrictions on the change of heat into work, whereas (6) deals with the flow of heat from hot to cold parts of a body. The Clausius-Duhem inequality appears to combine these two ideas into one inequality. In this respect, it represents a weaker physical statement than the separate inequalities (6) and (11) but only for the special class of materials defined by $(15)_{1,2}$. When (15) does not hold, the inequalities (6) and (11) do not imply the Clausius-Duhem inequality. Elsewhere [3] the present authors have demonstrated by specific examples some shortcomings of the Clausius-Duhem inequality in certain dissipative materials including the fact that it may lead to the possibility of perpetual motion of the second kind, whereas the inequality (11) denies such a perpetual motion.

Still continuing with the class of materials specified by (15), we see from (11) and (8) that

$$Q(\mathcal{B}_t) = \int_{\mathcal{B}_t} (\theta \dot{\eta}' - w) dm \quad . \tag{20}$$

In a cycle in which η' is periodic and has the same value at the beginning and end of the cycle, $\dot{\eta}'$ must have some negative values over a nonempty part of the period. Hence, using also the inequality (11), we have

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and we conclude that the body must always emit heat. It follows that the Statements 1 and 2 now hold without making use of the heat conduction inequalities (5) and (6).

Turning to more general materials for which the restrictions (15) and (16) do not hold, it was pointed out above that Fosdick and Serrin and Truesdell have proved the Statements 1-4 using the global Clausius-Duhem inequality, as well as the heat transfer inequalities (5) and the cyclic conditions (17). This is an extremely strong result mainly because of the use of the Clausius-Duhem inequality and the cyclic conditions $(17)_{2,3}$. As Truesdell remarks [2, p. 287], perhaps this inequality expresses more than the second law, although as noted above the Clausius-Duhem inequality may in some respects be too weak. The possibility that the Clausius-Duhem inequality expresses more than the second law has been illustrated by Green and Naghdi [3]. By a specific example, which is concerned with a rigid heat conductor in a state of thermal equilibrium and subjected to a spatially homogeneous temperature distribution, they show (see Example 2 in section 7 of [3]) that the Clausius-Duhem inequality requires that heat <u>added</u> to the conductor give rise to a <u>decrease</u> in temperature. It also denies the possibility that heat, in a theory which is linearized about a constant equilibrium temperature, can propagate with a finite wave speed.

If one imposes the restrictions that for a cycle

$$\Delta K = 0 \quad , \quad \Delta E = 0 \quad , \quad \Delta H^* = 0 \quad , \tag{22}$$

then the Statements 1-4 can still be proved with the use of the inequality (11) of Green and Naghdi, together with the conditions (5) and (6). However, it is clear that the conditions $(22)_{1,2}$ for cyclic motions are very severe and we do not impose these conditions.

10.

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This paper is concerned with the implications of an inequality proposed recently by Green and Naghdi [3] in regard to the classical statements of the second law of thermodynamics associated with cyclic thermo-mechanical processes. The results obtained are compared with corresponding previous developments by Fosdick and Serrin [1] and by Truesdell [2] who employ the Clausius-Duhem inequality.

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